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# Investigation on effect of aggregate on three non-destructive testing properties of concrete subjected to sulfuric acid attack

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## HIGHLIGHTS

- Dynamic modulus loss can be used to evaluate concrete sulfuric acid resistance.
- Advantage of calcareous aggregate was analyzed from the view of thermodynamics.
- Effect of fine aggregate on corrosion rate is more significant than coarse aggregate.
- The corrosion rate of concrete with two mineralogical types of aggregates were sorted.

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## ABSTRACT

In order to investigate the effect of aggregates on the concrete sulfuric acid resistance, accelerated corrosion experiments were conducted with four types of concretes composed of coarse and fine aggregates with two different chemical compositions. All the concretes with the same water/cement ratio of 0.45, and the pH value was kept in the range of 0.93–0.97. With continuous monitoring of each concrete specimen, corrosion depth, mass loss, and dynamic modulus elasticity loss were calculated. The results showed that the dynamic modulus of elasticity loss can be regard as an acceptable indicator for evaluating the resistance of concrete to sulfuric acid attack as well as corrosion depth and mass loss. A regression model proposed in this paper could provide good predictions. Concrete with marble aggregates rich in calcium carbonate have better performances in sulfuric acid solution than that with inert aggregates. Effect of fine aggregate on concrete sulfuric acid corrosion rate is more significant than coarse aggregate in the term of corrosion depth, mass loss, and dynamic modulus of elasticity loss.

## 1. Introduction

It is recognized that the hydration products of Portland cement concrete are alkaline and the pore solution in the concrete typically has a pH value ranging between 12 and 13.5. So it cannot be immune from acid attack. Owing to the spread of concrete structures damages in both urban and industrial areas, concrete acidic attack has attracted more and more attention in recent years. Sulfuric acid is the most widely distributed acid medium in the environment. Sulfuric acid can be generated from the oxidation of sulfide minerals (e.g. pyrite) [1]. Sulfuric acid is also a chief component of acid rain. It is reported that acid rain falls cover at least one third of Chinese territory [2]. Moreover, biogenic sulfuric acid corrosion is a common type of damage in sewage pipe systems [3,4]. It is estimated that costs of maintenance and repair due to sulfuric acid attack are several ten billion dollars in U.S. on sewer systems, which are even more than the costs of constructing new wastewater structures [5,6]. Hence there is an urgent need to investigate the deterioration rules of sulfuric acid attack on concrete structures in order to minimize its impact. Several researchers [6–9] have studied the effect of cement type, cement content, water-to-cementitious materials ratio on improving the resistance of mortar or concrete to sulfuric acid attack. It has also been reported that the use of supplementary cementitious materials (SCM) such as silica fume, fly ash, blast furnace slag, limestone filler, and natural pozzolana in concrete has improved the resistance of concrete to sulfuric acid attack because of its finer pore structure and the reduced presence of calcium hydroxide, which is most vulnerable to acid attack [10–13]. But, aggregate consists 65–80 percent of concrete proportion and has the main role in concrete behavior such as durability, dimensional stability and workability [3,14]. Therefore, it appears necessary to better understand the

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deterioration mechanisms associated with aggregate when concrete subjected to sulfuric acid attack. According to the mineralogical composition, aggregate can be divided into two types: one type is calcareous aggregate which is rich in calcium carbonate and is more vulnerable to acid attack. The other type is siliceous aggregate which is rich in silicon dioxide and is more resistant to acid attack. Which type of aggregates should be chosen in the acid environment remains controversial. Some researchers are convinced that aggregate is the main component of the concrete, and the concrete corrosion process will be accelerated if the aggregate is damaged by the acid first [15]. However, other researchers have published results that concrete with coarse calcareous aggregate offers better resistance to sulfuric acid attack. Hughes et al. [16] reported that the mass loss of cubes with limestone coarse aggregate and siliceous sand was less than that with limestone coarse and fine aggregates. In his study, only the mass loss and visual inspection were researched and just three combinations of coarse and fine aggregates were adopted in concrete without the cubes with siliceous coarse aggregate and limestone fine aggregate. Belie et al. [17] found that the aggregate type had the largest effect on concrete degradation after sulfuric acid corrosion. Concrete with limestone aggregates showed a smaller degradation depth than that with inert aggregates. Chang et al. [18] presented that concrete made with limestone aggregates and the ternary cement containing 7% silica fume and 33% fly ash has an excellent acid resistance in 1% sulfuric acid solution. The fine aggregate used in his study was only silica river sand. Bederina et al. [19] pointed out that the mass loss in the case of limestone sand is lower than that of silica sand mortar when exposed to hydrochloric acid solution. However, an extensive review of literature indicates that the significance of coarse and fine aggregate on the concrete sulfuric acid corrosion is not clearly clarified. In order to explore the question that which has greater influence on the concrete sulfuric acid resistance, coarse aggregate or fine aggregate, concretes with four different combinations of aggregates were adopted in the accelerated sulfuric acid corrosion test. In previous studies, mass loss and corrosion depth were regarded as acceptable indicators for evaluating the resistance of concrete to sulfuric acid attack. In this paper, in addition to the above two indicators, dynamic modulus of concrete after sulfuric acid corrosion was also measured through impact resonance test, which is a non-destructive testing method.

## 2. Experimental investigation

### 2.1. Raw materials

Local Portland cement (P·II 52.5R) with a 28d compressive strength of 55.3 MPa was used, which complies with Chinese standard GB175-2007 and is similar to ASTM C150 type I cement [20]. The specific gravity of the cement was 3.1. River sand and gravel were used as fine and coarse siliceous aggregates, which come from a local pipe pile corporation at Suzhou in China. Crushed marble sand and stone were used as fine and coarse calcareous aggregates, which come from a whole rock block bought at a stone market in Shanghai, China. The phases for gravel and marble were tested with X-ray fluorescence (XRF), and the results are listed in Table 1. Because the main composition of the marble was calcium oxide (CaO) as shown in Table 1, marble stone and sand can be classified into calcareous aggregates category. Since the river sand is mainly composed of silicon dioxide (78.56% in Ning Y.'s paper [21] and 88.54% in Limbachiya M.'s paper [22]), the gravel and river sand can be classified into siliceous aggregates category.

Gravels with a maximum nominal size of 25 mm. and water absorption of 0.92% were obtained for concrete specimens. Table 2 shows the particle size gradation of gravel (coarse aggregates) used in the trial mixture. Natural river sand (fine aggregates) with a fineness modulus of 2.61 and water absorption of 1.79% was used for concrete specimens. Table 3 shows the particle size gradation of river sand used in the trial mixture.

Marble stone and sand, cut from the same parent natural rocks, were made into crushed stones by a crusher and were subsequently divided into 9 kinds of particle sizes by a sieve shaker sized 0.15–0.3 mm, 0.3–0.6 mm, 0.6–1.18 mm, 1.18–2.36 mm, 2.36–4.75 mm, 4.75–9.5 mm, 9.5–16 mm, 16–19 mm, 19–26.5 mm. These crushed marble stones were used as coarse and fine calcareous aggregates. In order to accommodate marble stone and sand with the gravel and river sand in the aspect of aggregate gradation, the mass percentages of marble stone sized 2.36–4.75 mm, 4.75–9.5 mm, 9.5–16 mm,16–19 mm,19–26.5 mm were 4%, 19%, 30%, 22%, 25% (Data from Table 2), respectively. The mass percentages of marble sand sized 0.15–0.3 mm, 0.3–0.6 mm, 0.6–1.18 mm,1.18–2.36 mm,2.36–4.75, 4.75–9.5 mm were 9.2%, 44.4%, 17.8%, 10.2%, 10.8%, 5.6% (Data from Table 3), respectively.

### 2.2. Mixture design

In this paper, the specimens were divided into four groups denoted by C1F1, C1F2, C2F1, and C2F2.The coarse and fine aggregates of C1F1 were gravel and river sand, C1F2 were gravel and crushed marble sand, C2F1 were crushed marble stone and river sand, and C2F2 were crushed marble stone and marble sand, respectively. The water/cement ratio were 0.45 (by weight), and the mass ratio of fine aggregate to total aggregate was 0.31 for all mixture proportions. Tap water with ambient temperature was used. The apparent density of gravel, river sand, marble stone, marble sand were 2644 kg/m$^3$, 2540 kg/m$^3$, 2575 kg/m$^3$, 2630 kg/m$^3$, respectively. Mix proportions for concrete specimens are given in Table 4. Naphthalene based superplasticizer was added to obtain sufficient workability. The mass ratio of superplasticizer to cement was 0.6%. The compressive strength at 28 days before corrosion is designed to be approximate 45 Mpa.

### 2.3. Experiment design

#### 2.3.1. Twelve specimens preparation

Although both cylindrical specimen and prismatic specimen can be tested, the prism corners will suffer more severe damage than that of lateral plane in the corrosion environment. So the cylindrical specimen was chosen in this study. Concrete was mixed in the laboratory using an electric mixer. Freshly mixed concrete was casted into cylinder steel molds, which were 100 mm in diameter by 200 mm in height, and then compacted on a vibration table.

**Table 1**
Chemical composition of two types of aggregates (% by mass).

| Constituent | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | MgO | CaO | $Na_2O$ | $K_2O$ | $P_2O_5$ | $CO_3$ |
|---|---|---|---|---|---|---|---|---|---|
| Gravel | 59.323 | 14.923 | 4.089 | 1.134 | 3.487 | 4.449 | 3.914 | nd | 7.831 |
| Marble | nd | nd | 0.028 | nd | 56.636 | 0.002 | 0.008 | 0.034 | 44.134 |
| Sand [21] | 78.56 | 7.02 | 2.58 | 0.78 | 3.66 | 1.51 | 1.39 | nd | nd |

*Note: nd means content is lower than the limit of detection.